THE UNIVERSITY of EDINBURGH

Edinburgh Research Explorer

Phonon softening and lattice melting at the ferroelastic phase transition in Na2CO3

Citation for published version:
Harris, M, McMorrow, DF & Godfrey, KW 1997, 'Phonon softening and lattice melting at the ferroelastic phase transition in Na2CO3', *Physical Review Letters*, no. 79, pp. 4846-4849. https://doi.org/doi:10.1103/PhysRevLett.79.4846

Digital Object Identifier (DOI):
doi:10.1103/PhysRevLett.79.4846

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published In:
Physical Review Letters

Publisher Rights Statement:
©Harris, M., McMorrow, D. F., & Godfrey, K. W. (1997). Phonon softening and lattice melting at the ferroelastic phase transition in Na2CO3. Physical Review Letters, (79), 4846-4849doi: doi:10.1103/PhysRevLett.79.4846

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

OPEN ACCESS

Download date: 05. May. 2023

Phonon Softening and Lattice Melting at the Ferroelastic Phase Transition in Na_2CO_3

M. J. Harris,[1] D. F. McMorrow,[2] and K. W. Godfrey[3]
[1]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX, United Kingdom*
[2]*Department of Solid State Physics, Risø National Laboratory, DK-4000 Roskilde, Denmark*
[3]*Oxford Physics, Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, United Kingdom*
(Received 6 June 1997)

We present the results of a detailed inelastic neutron scattering study of the dynamics of the ferroelastic phase transition in Na_2CO_3. The driving instability is a transverse acoustic mode that softens over a plane of wave vectors, resulting in a continuous loss of long-range order, in accord with theoretical predictions. At T_c a wide distribution of excitations is observed in the plane of critical wave vectors, similar to the dynamics of a liquid. Perpendicular to this plane the system possesses one-dimensional order. [S0031-9007(97)04792-3]

PACS numbers: 64.70.Dv, 61.12.Ex, 63.70.+h

Two of the most common, but elusive, physical phenomena are the melting of a solid and the inverse, its crystallization from a liquid. The bulk features of the two processes are easily quantifiable, but comprehensive microscopic descriptions have yet to be obtained. While melting is a cooperative phenomenon and must therefore be mediated by the lattice dynamics, it is not clear whether the instability is a bulk effect, or is precipitated by premelting at surfaces or defects [1]. A difficulty associated with experimental studies of melting is that it is strongly discontinuous, meaning that it is impossible to get close enough to the transition to detect the onset of the driving instability before it actually occurs.

One of the most striking related discoveries in recent years is that of lattice melting, where a crystalline solid undergoes a process of *continuous* melting at a structural phase transition, only to recrystallize after the transition is passed [2,3]. This has only been observed unambiguously in a single material so far, Na_2CO_3, although it is thought also to occur in K_2CO_3 [4]. The transition in both materials is ferroelastic in character, driven by transverse acoustic modes that soften over a whole *plane* of wave vectors. This means that the order parameter is two dimensional ($m = 2$), and a mean-field theory of the transition requires logarithmic corrections, indicating that the mean-squared atomic displacements diverge logarithmically at T_c [2,3]. This causes a complete breakdown of the long-range order, in common with a conventional solid-to-liquid transition, although in lattice melting the transition can be continuous, which is in fact the case for Na_2CO_3. This presents the fascinating possibility of being able to enter the transition state continuously, so as to characterize the mechanism that drives the loss of long-range order.

Detailed neutron diffraction studies have been performed of the structure of Na_2CO_3 as it undergoes the ferroelastic transition [4–6]; the transition produces a continuous hexagonal-monoclinic symmetry change ($P6_3/mmc - C2/m$) with $T_c \sim 755$ K. The crystal structure of the hexagonal phase contains one-dimensional chains of NaO_6 face-sharing octahedra lying parallel to the **c** axis. These chains are linked laterally to each other by carbonate groups, which act as "hinges" so that the chains can shear against each other along the **c** axis. As the crystal is cooled towards T_c the restoring force for the shears becomes smaller and smaller, and shear fluctuations of the chains become larger. At the critical temperature, the amplitude of these fluctuations diverges, while below it they freeze in to produce a static monoclinic strain. The shear fluctuations are the soft transverse acoustic modes with wave vectors in the $\mathbf{a}^*$-$\mathbf{b}^*$ plane and eigenvectors parallel to the **c** axis. Hence, the process of lattice melting is largely a divergence of the mean-squared atomic displacements parallel to the **c** axis.

Theoretical predictions for the x-ray and neutron diffraction patterns [7] indicate that the loss of long-range order at T_c destroys the usual delta-function Bragg peaks, and replaces them with diffuse scattering with a power-law distribution. This is similar to the scattering from two-dimensional systems such as smectic liquid crystals [8], where the acoustic modes destroy long-range order. The neutron diffraction results from Na_2CO_3 are fully in accord with these predictions, but also indicate that it undergoes a special form of lattice melting, where the long-range order is only destroyed in a two-dimensional sense, but is effectively preserved in the third dimension, which in this case is the **c** axis. This indicates that, while the ordered correlations transverse to the NaO_6 chains are lost at T_c, the structure of each chain itself is preserved.

While the structural aspects of the phase transition are well understood both theoretically and experimentally, the same cannot be said of the dynamics. One of the most intriguing open questions is the character of the lattice dynamics at the critical point, since long-range order is completely destroyed and strictly there is no lattice. In this Letter we present a detailed inelastic neutron scattering study of the soft acoustic phonons in Na_2CO_3, concentrating on the transition state. We show that the inelastic spectrum at T_c bears a striking similarity with the

 0031-9007/97/79(24)/4846(4)$10.00 © 1997 The American Physical Society

neutron scattering expected from a classical liquid, where it arises from a combination of large-scale diffusional and local vibrational motions.

Our inelastic neutron scattering measurements were performed using the TAS7 triple-axis neutron spectrometer at Risø National Laboratory. Pyrolytic graphite crystals were used for both monochromator and analyzer, and the analyzing energy was kept fixed at 4.9 meV; the corresponding energy resolution was 0.2 meV (FWHM). A cooled beryllium filter was placed in the scattered beam to reduce higher-order contamination. We used a single crystal of Na_2CO_3 (with a volume of approximately 4 cm^3) which was aligned with the $\mathbf{a}^*$-$\mathbf{c}^*$ plane of reciprocal space in the scattering plane of the spectrometer. As the crystal is cooled through the ferroelastic transition into the low-temperature monoclinic phase, ferroelastic twinning occurs, which causes each (0 0 l) Bragg peak to split continuously into two components in a single crystal. By scanning in wave vector across the (0 0 2) Bragg position while heating towards the phase transition, we determined the temperature where the splitting disappears completely as $T_c = 752(1)$ K.

As the transition is approached, the transverse acoustic branch softens for all wave vectors in the $\mathbf{a}^*$-$\mathbf{b}^*$ plane, so that at T_c the entire branch has collapsed to zero energy from the Brillouin zone center right out to the zone boundary. We characterized the softening by performing constant-Q scans at the (0.1 0 2) position between 763 and 923 K. Between T_c and 763 K, the softening of the acoustic mode is so great that, within the limits of the experimental resolution, it could not be distinguished from purely quasielastic scattering centered on zero energy transfer. In order to obtain the phonon energy, each constant-Q spectrum was fitted to the spectral response of a damped harmonic oscillator convoluted with the experimental resolution function, calculated using the method of Popovici *et al.* [9]. Representative spectra with the results of the fitting procedure are shown in Fig. 1. Strong elastic scattering occurs in all of the spectra measured at the (0.1 0 2) point, which is a mixture of incoherent scattering and Bragg contamination due to the proximity of the (0 0 2) Bragg peak. At high temperatures, the acoustic mode appears as a well-defined inelastic peak, but as the crystal is cooled towards the transition, the phonon energy decreases so that the peak begins to merge with the elastic scattering. Our fits revealed that no significant change occurs in the phonon damping as the transition is approached. Therefore, the problem of separating the acoustic mode from the elastic signal is mainly one of instrumental resolution, which in this case was very good, so that we were able to measure the phonon softening much more precisely than a previous preliminary study [6].

The temperature dependence of the soft elastic constant C_{44}, obtained from the dispersion of the soft acoustic mode at the (0.1 0 2) point, is plotted in Fig. 2. Renormalization-group calculations [2,3] predict that C_{44}

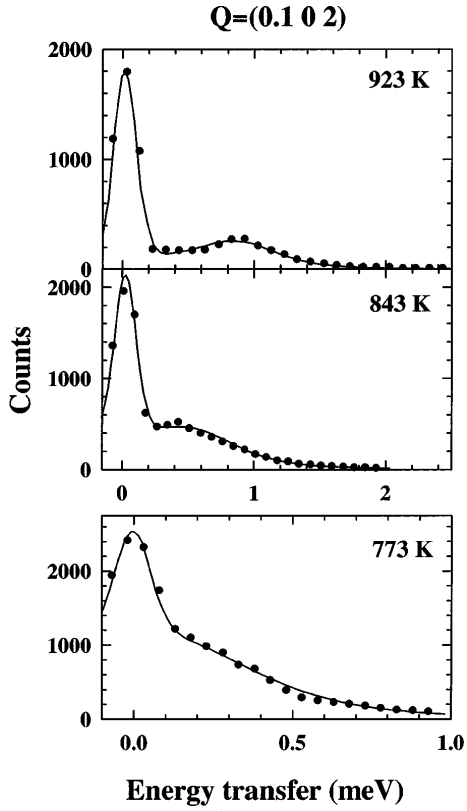

FIG. 1. Constant-Q scans through the (0.1 0 2) point in Na_2CO_3 at 923, 843, and 773 K, illustrating the softening of the transverse acoustic mode as the transition is approached ($T_c = 752$ K). The strong elastic component in all spectra is due to incoherent and contaminant Bragg scattering, and the curves show fits to the data of a damped harmonic oscillator convoluted with the experimental resolution.

should behave as

$$C_{44} \propto \tau[\ln \tau]^{-1/3}, \tag{1}$$

where $\tau = (T - T_c)/T_c$ and $T_c = 752$ K. The curve in Fig. 2 is a fit of this expression to the experimental data. The agreement is good, providing further validation for the logarithmic corrections to mean-field theory which predict the effect of lattice melting. By contrast, the standard mean-field result $C_{44} \propto \tau$ provides a poor description of the data.

In addition, we performed constant-Q scans at several points along the (0 0 l) direction in order to survey the temperature-dependent behavior of the longitudinal acoustic mode. We observed that the dispersion of the mode increases as the crystal is cooled towards T_c. In addition, no change in its damping occurs at T_c, and we conclude that its behavior is noncritical and entirely independent of the phase transition. However, this is not entirely surprising since the longitudinal mode involves only compressions of the octahedral chains along their lengths, and neutron diffraction work shows that their structural integrity is unaffected by the transition [6].

We now discuss our detailed measurements of the line shape of the soft transverse acoustic branch at the critical

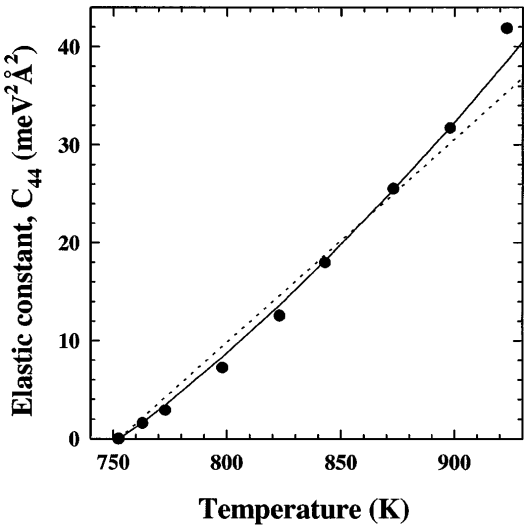

FIG. 2. The temperature dependence of the soft elastic constant, C_{44}, obtained from the dispersion of the soft transverse acoustic mode measured at the (0.1 0 2) point. The errors are smaller than the size of the data points, and the curve is a fit to the data of the renormalization-group prediction for C_{44}, Eq. (1). For contrast, the dotted line shows the poorer fit to the data obtained with the standard mean-field result, $C_{44} \propto \tau$.

point. In Fig. 3 we show constant-Q scans across the branch from the (0.1 0 2) point out to the (0.4 0 2) point [13], measured at $T_c = 752$ K. The inelastic scattering is clearly quasielastic in nature in all of these scans, and there is no evidence for a central peak, since the elastic scattering is at the same level as in the high-temperature scans, and is thus purely incoherent in origin. On the other hand, a central peak has been observed in the ferroelastic mixed system KCN:KBr [10], probably reflecting frozen-in shear strains due to the presence of orientational and positional disorder of the CN^- and Br^- ions. Na_2CO_3 is a much more ideal system for the purpose of studying lattice melting, because it is very pure and free from defects of this kind. It should be noted that the inelastic scattering from Na_2CO_3 at T_c extends over several decades of intensity, and also over a relatively large energy range (up to at least 6 meV, which was the maximum accessible energy transfer with our spectrometer configuration). This is in stark contrast to the behavior that would be observed in a three-dimensional crystal, and instead is highly reminiscent of liquidlike dynamics.

Attempts were made to fit the quasielastic scattering with a variety of models, such as those with Lorentzian and exponential distributions. The most satisfactory fit to the experimental data was obtained using the model due to Egelstaff and Schofield [11]. This model was developed for describing the inelastic neutron scattering from liquids, and, in particular, the quasielastic scattering resulting from diffusional motion of atoms through the system. A simple theory of diffusion predicts that the quasielastic scattering should have a Lorentzian distribution, but this neglects the fast vibrational processes that occur between

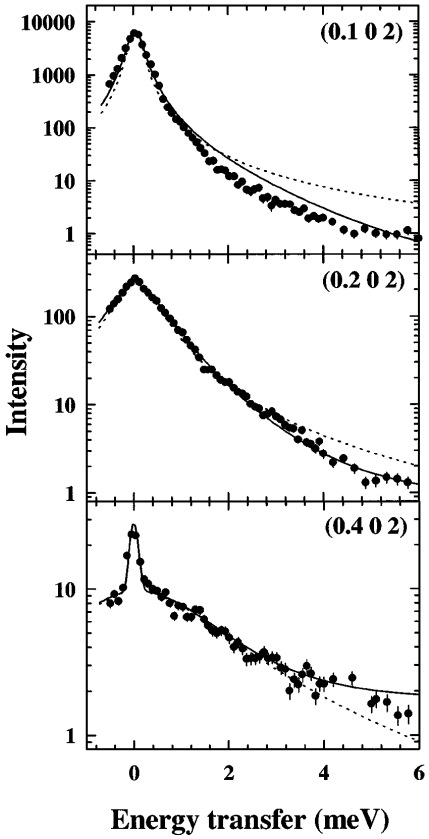

FIG. 3. Constant-Q scans through the transverse acoustic mode at the critical temperature, $T_c = 752$ K. The full curves show fits of the Egelstaff-Schofield model, Eq. (2), convoluted with the experimental resolution function. For comparison, the dotted curves show fits of a Lorentzian function convoluted with the resolution. The sharp elastic component in the (0.4 0 2) data is due to incoherent scattering. Note that the intensity scale is plotted logarithmically to illustrate the smooth spread of inelastic scattering over several decades of intensity.

diffusional jumps of the atoms. For illustration, the dotted curves in Fig. 3 show fits with the simple Lorentzian model, which gives a poor description of the data at high energies. The problem is that, while for long times t, the mean-squared atomic displacements are $\langle u^2(t)\rangle \propto |t|$, for short times $\langle u^2(t)\rangle \propto t^2$. Egelstaff and Schofield's model accounts for this by fabricating a simple functional form for the velocity autocorrelation function that joins the two forms asymptotically. The neutron scattering cross section is then

$$S(Q,\omega) \sim \exp\left(\frac{\hbar\omega}{2k_BT} + \Delta\right)\frac{c\Delta}{(\omega^2 + \Delta^2)^{1/2}} \times K_1[c(\omega^2 + \Delta^2)^{1/2}], \quad (2)$$

where Q and $\hbar\omega$ are the neutron wave vector and energy transfer, respectively, Δ is the effective wave-vector-dependent width of the quasielastic scattering, K_1 is the modified Bessel function of the second kind, and c is a measure of the time that elapses during which the atoms vibrate about their initial positions before a diffusional event. The full curves shown in Fig. 3 are fits to the data

of this model. Initial fits were made to all spectra in order to determine the best value of c, which is 0.56(5) meV^{-1} [12]. Once c had been determined, more careful fits were made, with the following parameters allowed to vary in the model: a flat background, a center to allow for slight offsets in the calibration of the spectrometer, an overall scale factor, and Δ. The agreement with the measured spectra is generally good.

The Egelstaff-Schofield model was originally developed for liquids, where the width parameter is given as $\Delta = Q^2D$ (where Q is the wave vector transfer and D is the diffusion coefficient). In Fig. 4 we show the extracted values of $\Delta^{1/2}$ plotted against the reduced wave vector $\mathbf{q} = (h\ 0\ 2)$. $\Delta^{1/2}$ is linear with $\mathbf{q}$ until beyond the point $h = 0.3$, where it decreases from a linear dependence and turns over at $h = 0.5$, which is a zone boundary point of the high and low temperature phases [13]. The initial linear dependence of $\Delta^{1/2}$ is suggestive of the simple diffusion law frequently observed in liquids (i.e., $\Delta^{1/2} \propto Q$). However, in a true liquid the wave vector Q refers to the *total* wave vector transfer measured from the only Γ point present, i.e., (0 0 0), and the structure factor is then finite for all nonzero values of Q. Although the long-range order is destroyed at T_c in Na_2CO_3, it is only destroyed in a "weak" sense [7,14], as there is still a divergence of the structure factor. The divergence is that of a power law rather than the delta-function characteristic of true long-range order. A power law reflects the fact that short-range periodic correlations exist transverse to the chains, and the $\mathbf{q}$ dependence of Δ must reflect this periodicity. Note that, in the analogous case of jump diffusion in a periodic lattice, the quasielastic energy width has the lattice periodicity (see, for example, Goff *et al.* [15]). In Na_2CO_3, the diffusional process is not that of single particles jumping from one site to another, but instead is related to large-scale shears of whole chains of NaO_6 octahedra along the **c** axis. In effect, the amplitude of the shears is so large that, on the time scale of our inelastic neutron scattering experiment, the chains act as though they are moving slowly through a viscous medium. This observation brings out the similarity between the processes of lattice melting and conventional melting, which is that they are both controlled by large-amplitude shear fluctuations which destroy long-range order.

It is interesting to note that, while this extreme thermal motion fulfills the Lindemann criterion for melting, the chains retain their integrity along the **c** axis perfectly. The upshot is that there is full long-range order for correlations purely along the length of each chain. This brings out the unusual nature of the transition state in Na_2CO_3, which possesses simultaneously, characteristics of a fully ordered crystal, a liquid crystal, and a conventional liquid. In effect, it represents a state intermediate between these three.

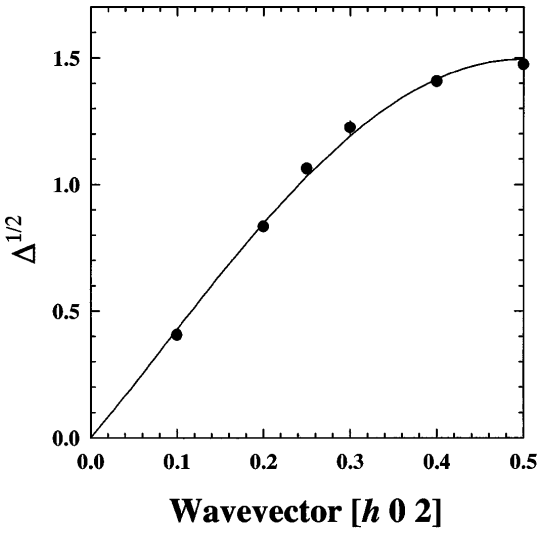

FIG. 4. The square root of the effective quasielastic width parameter Δ plotted against reduced wave vector $\mathbf{q} = (h\ 0\ 2)$. The curve is a guide to the eye.

We wish to thank P. Schofield, P. A. Lindgård, S. W. Lovesey, M. T. Dove, J. P. Goff, R. A. Cowley and S. T. Bramwell for helpful discussions. We acknowledge the support of the EPSRC and the European Commission through the Training and Mobility of Researchers Programme.

[1] L. L. Boyer, Phase Transit. **5**, 1 (1985).
[2] R. A. Cowley, Phys. Rev. B **13**, 4877 (1976).
[3] R. Folk *et al.*, Z. Phys. B **25**, 69 (1976); Phys. Lett. **57A**, 112 (1976); Phys. Rev. B **20**, 1229 (1979).
[4] I. P. Swainson *et al.*, J. Phys. Condens. Matter **7**, 4395 (1995).
[5] M. J. Harris *et al.*, Phys. Rev. Lett. **71**, 2939 (1993); Phys. Rev. B **51**, 6758 (1995).
[6] M. J. Harris *et al.*, J. Phys. Condens. Matter **8**, 7073 (1996).
[7] A. P. Mayer and R. A. Cowley, J. Phys. C **21**, 4827 (1988).
[8] J. Als-Nielsen *et al.*, Phys. Rev. B **22**, 312 (1980).
[9] M. Popovici, A. D. Stoica, and I. Ionita, J. Appl. Crystallogr. **20**, 90 (1987).
[10] K. Knorr *et al.*, Phys. Rev. Lett. **55**, 2445 (1985).
[11] P. A. Egelstaff and P. Schofield, Nucl. Sci. Eng. **12**, 260 (1962).
[12] This value is typical of those also observed in liquid metals such as Na and Pb [S. J. Cocking, J. Phys. C **2**, 2047 (1969)].
[13] To set the scale, the hexagonal lattice parameters just above T_c are $a = 5.2$ Å and $c = 6.5$ Å.
[14] H.-J. Mikeska and H. Schmidt, J. Low Temp. Phys. **2**, 371 (1970).
[15] J. P. Goff *et al.*, J. Phys. Condens. Matter **4**, 1433 (1992).